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Enhanced field emission of an electric field assisted single-walled carbon nanotube assembly in colloid interstices

Young Koan Ko[a,1], *Jianxin Geng*[a,1], *Se-Gyu Jang*[a], *Seung-Man Yang*[a], *Tae Won Jeong*[b], *Yong Wan Jin*[b], *Jong Min Kim*[b], *Hee-Tae Jung*[a,*]

[a] *Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, 373-1 Guseong-dong, Yuseong-gu, Daejeon 305-701, Republic of Korea*
[b] *Display Device and Materials Lab., Samsung Advanced Institute of Technology, P.O. Box 111, Suwon 440-600, Republic of Korea*

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ABSTRACT

A novel method for fabrication of vertically aligned single-walled carbon nanotubes (SWCNTs) on indium–tin oxide glass substrates modified with self-assembly monolayer has been developed by using a supporting frame composed of a monolayer of monodispersed silica beads and an alternating current electric field. We have found that SWCNTs can be implanted into the interstices of the colloidal superlattices, which function as supporting scaffold to prevent the SWCNTs from falling down and maintain the SWCNTs at low density. As a result, this vertically aligned SWCNT assembly exhibits enhanced field emission.

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1. Introduction

The use of single-walled carbon nanotubes (SWCNTs) as field emission source is one of the most promising aspects among SWCNT-based applications [1–8]. In the application of carbon nanotubes (CNTs) to field emission display (FED), many efforts have been made to prepare vertically aligned CNTs on a large scale. Vertically aligned CNT films can be prepared by chemical vapor deposition (CVD) [9–13]. In order to obtain free-standing CNTs, substrate bias generated by applied direct current (DC) [14,15], magnetic field [16], or porous alumina templates [17] have been integrated into the thermal CVD method. As a typical paradigm, freestanding CNT arrays were synthesized on Ni dot arrays by DC plasma-enhanced CVD [18,19]. However, both the direct and the modified CVD methods show disadvantages in the high temperature (850–1000 °C) required in synthesis and the remaining of catalyst residue in the resultant vertically aligned CNT films or arrays.

As a post-treatment approach, screen-printing is commonly used to fabricate SWCNT cathodes for FEDs [20–22], but this approach still suffers from short lifespan of the FED devices and low resolution due to the ununiformity of SWCNTs and organic contaminants. As an alternative post-treatment approach, self-assembly method is easy and shows promising prospect for preparing vertically aligned SWCNTs at room temperature. Several self-assembly methods such as chemical assembly onto various surfaces have been used to prepare SWCNT films [23,24]. Although this method has great potential for the surface modification and functionalization with SWCNTs, the alignment degree of the resulting SWCNTs is not sufficient for practical applications, which results in low emission performance.

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[*] *Corresponding author:* Fax: +82 42 350 3910.
E-mail address: heetae@kaist.ac.kr (H.-T. Jung).
[1] Both authors are equally contributed to this work.

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In this paper, we present a novel self-assembling method, which makes use of a colloidal monolayer as supporting frame in the presence of an alternating current (AC) electric field, for preparing vertically aligned SWCNTs in the application of high-efficient FED devices. It is shown that the interstices of the colloidal particle assembly can maintain the vertical alignment of the SWCNTs after the electric field is removed. This method affords vertically aligned SWCNTs on self-assembly monolayer (SAM) modified indium–tin oxide (ITO) substrates at room temperature, resulting in highly efficient use of SWCNTs and large area deposition of SWCNTs. The field emission property was characterized, and the field emission devices prepared by using these SWCNT assemblies exhibit high performance in field emission property.

2. Experimental

2.1. Purification and treatment of SWCNTs

As-prepared SWCNTs (HiPco, Carbon Nanotechnologies Inc.) were purified and end functionalized by using hydrochloric acid and piranha solution, respectively [25,26]. Before the end functionalization process, the purified SWCNTs were annealed at 800 °C for 1 h under the protection of Ar in order to reduce the defect content on the side-wall surfaces. The end functionalized SWCNTs were dispersed in *N,N*-dimethylformamide (DMF) (20 mg L^{-1}) by ultrasonication for 4 h. The solution was centrifuged at 15,000 rpm for 90 min to separate the high-efficiently dispersed SWCNTs from the SWCNT bundles; the supernatant was decanted for characterization and fabrication of field emission devices.

2.2. Preparation of colloidal silica spheres

SiO_2 spheres with diameters ranging from 280 to 730 nm were synthesized with the Stöber method via a sol–gel reaction of silicon alkoxide, i.e., tetraethylorthosilicate (TEOS) [27], and a modified seeded-growth procedure originally described by Zhang et al. [28] A typical procedure was as follows: 0.5 mL of TEOS was rapidly mixed with 2 mL of ethanol; the TEOS solution was added to a mixture solution of ethanol and NH_4OH (100 mL of ethanol and 20 mL of NH_4OH (28–30%, Merck)), followed by stirring for 2 h at room temperature. The resultant suspension contained particles of approximately 300 nm in diameter. Using these particles as seeds, larger silica particles were synthesized by further addition of TEOS into the reaction system. Unreacted precursors were removed by solvent exchanging: the particles were retrieved by centrifuging at 3000 rpm and redispersed in deionized water by ultrasonication. Silica spheres with diameter of 280, 570, and 730 nm were synthesized. Finally, the silica spheres were redispersed in ethanol with a concentration of 10 wt% for future usage.

2.3. Preparation of FED devices

In this study, three substrates were used to prepare SWCNT assemblies, i.e., 2-carboxyethyl phosphonic acid (2-CPA) SAM-modified ITO, amino-silanized ITO, and colloidal particle covered and 2-CPA modified ITO surfaces. Fig. 1 shows a self-assembling approach for preparing SWCNT assembly cathode by using the colloidal particle covered and 2-CPA modified ITO substrate. After successively cleaned with ultrasonication in chloroform, acetone, and 2-propanol, ITO surfaces were modified with 2-CPA, having a phosphonic head-group (–PO_3H_2) and a carboxylic acid tail (–COOH), by immersing the ITO substrates into a 5 mM 2-CPA solution in 2-propanol for 20 h, resulting in the formation of a 2-CPA SAM on ITO surfaces. And then monodispersed silica beads were spin coated on the 2-CPA modified ITO surfaces. Finally, SWCNT assembly cathode of FED device was prepared by electrophoresis deposition: 10 V of an AC electric field with a frequency of 10 KHz was applied across the colloidal particle coated ITO substrate (positively biased with an offset of 5 V) and a piece of bare ITO substrate (negatively biased), which were spaced out by insulating spacers (1 mm in thickness), after a SWCNT solution was injected into the space between the two electrodes. The AC voltage was kept until the solvent evaporated off. The SWCNTs can be driven to vertically align on the surfaces of the positively charged electrode under the induction effect of electric field [29], and immobilized in the interstices of the colloidal superlattices via the interactions between the 2-CPA SAM and the carboxylic acid groups on SWCNTs' ends. Moreover, the SWCNTs can be kept vertically standing with the supporting of the silica beads even after the electric field is removed, while the strong affinity between the SAM and the end-functional groups of the SWCNTs guarantees the robust attachment of the SWCNTs to ITO surfaces.

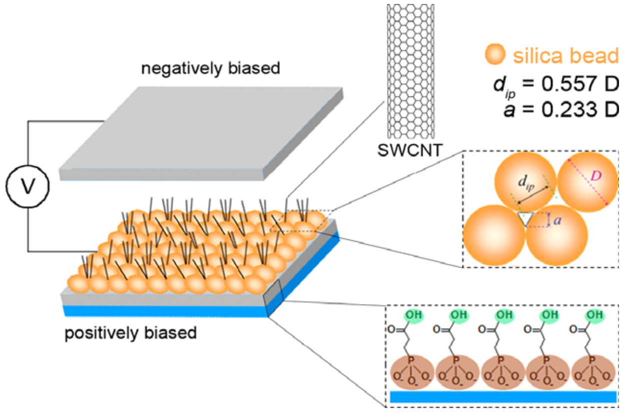

Fig. 1 – Illustration of the electric field assisted self-assembling method for preparation of vertically aligned SWCNTs in the interstices of colloidal superlattices.

2.4. Instrumentation

Scanning electron microscopy (SEM) images were obtained on an FEI SIRION FE-SEM operated at 10 kV. Raman spectra were recorded on a Bruker RFS-100 Raman Spectrometer with an excitation wavelength of 1064 nm. Atomic force microscope (AFM) images were obtained using an SPA 3800 N microscope with a SPA-400 scanner. AFM samples were prepared by dropping the SWCNT DMF solution on ITO substrates, which were afterward covered with another piece of glass slide and dried on a hot stage at 80 °C for 1 h. Finally, the ITO slides were separated for AFM scanning. The AC voltage used to prepare the SWCNT assembly cathode was generated by a HAMEG Programmable Function Generator (HM 8130); in the process of electrophoresis deposition, a Tektronix Oscilloscope (TDS 380) was used to monitor the current. The field emission current was measured by using a high-voltage supply (Keithley 248) and picoampere meter (Keithley 486) at a base pressure of 2×10^{-6} torr. The field emission *I*–*V* curves were recorded after sweeping the voltage several times for aging the field emission devices.

3. Results and discussion

Raman spectroscopy was used to verify the dispersibility of the SWCNTs in DMF suspension with a concentration of less than 10 mg L^{-1}. For the efficiently dispersed SWCNTs in DMF solution, the radial breathing mode band shows an up-shift of 9 cm^{-1} with respect to the solid SWCNT sample: 189 cm^{-1} for the as-prepared and purified SWCNTs at solid state and 198 cm^{-1} for the functionalized SWCNTs dispersed in DMF (Fig. 2a). This up-shift upon debunding results from the decreased energy spacing of the Van Hove singularities in isolated tubes over the spacing in a rope [30], indicating that the interaction between the SWCNTs in the DMF solution is weaker than that of SWCNTs at solid state, i.e., the SWCNTs can exist in an isolated state in the DMF solution. The small change in the D-bands of the functionalized SWCNTs with respect to that of the as-prepared SWCNTs indicates that less structural modification on the side-walls of SWCNTs has been produced during the process of end functionalization. In addition, the dispersibility of the SWCNTs in DMF was further examined by AFM: AFM images show that the SWCNTs' diameter ranges from 1.2 to 3.0 nm, supporting that the SWCNTs are isolatedly dispersed in the DMF solution (Fig. 2b).

The SWCNT assembly was first electrophoresis-deposited on 2-CPA SAM-modified ITO surfaces, with no use of the colloidal superlattices. The 2-CPA SAM was designed to increase the affinity between the SWCNTs and the ITO glass substrate [31]. Although it is generally believed that –PO_3H_2 reacts with ITO surfaces via the formation of a strong ionic bond between the anionic phosphonic acid group and the cationic metal of ITO [32], the bonding nature remains debated [31]. In this work, the relatively stronger interaction between the SWCNTs and 2-CPA with respect to that between the SWCNTs and bare ITO surfaces was directly verified by the selective deposition of the SWCNTs onto 2-CPA line patterns (Supporting material S1). The cathodes of the FED devices were prepared by electrophoresis deposition of the SWCNTs onto the surfaces of 2-CPA SAM-modified ITO glass. On the induction effect of the AC electric field, the SWCNTs in the suspension move to the positively charged electrode and vertically aligned on the electrode surface, as an optical image shows in Fig. 3 [29].

SEM image shows that the SWCNTs cannot retain the vertical alignment after the electric field is removed (Fig. 4a). Field emission devices were prepared with this SWCNT-coated ITO substrate used as cathode, a phosphor-coated ITO glass used as anode, and alumina layer of 200 μm in thickness used as spacer between the cathode and the anode; and the devices fabricated with such SWCNT coated ITO substrates exhibit poor field emission property (Fig. 4b). We speculate that the vertical alignment of the SWCNTs could be influenced by two factors: the interaction intensity of the nanotubes with the substrate and an effect of supporting frame that prevents the nanotubes from falling down. The first effort to keep the SWCNTs vertically aligned was carried out by replacing the interaction between the 2-CPA and the SWCNTs with a chemical bonding (Supporting Material S2). Unfortunately, the vertical alignment of the SWCNT still cannot be reserved after the electric field is removed even though the strength of the chemical bonding between the SWCNTs and ITO surfaces is greater than that in the 2-CPA SAM case.

In order to keep the SWCNTs' vertical alignment after the electric field is removed a kind of scaffold is incorporated into this system. Close-packed colloidal particles (monodispersed silica beads of 570 nm in diameter) stacked onto the 2-CPA modified ITO surfaces are designed as a supporting frame (Fig. 5a) [33]; it is expected that the SWCNTs can be implanted into the interstices of the colloidal superlattices. As shown in

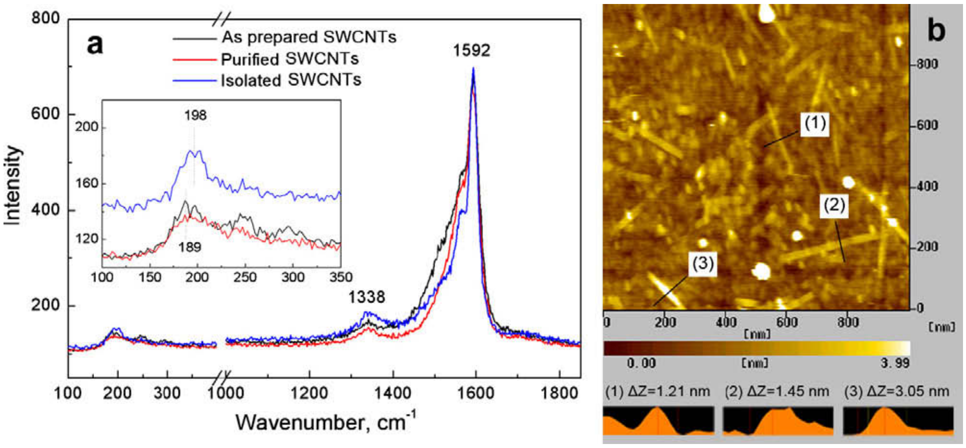

Fig. 2 – (a) Comparison of the Raman spectra of as-prepared and purified SWCNTs in solid state and the functionalized SWCNTs dispersed in DMF, (b) an AFM image of the isolated SWCNTs and the corresponding height profiles.

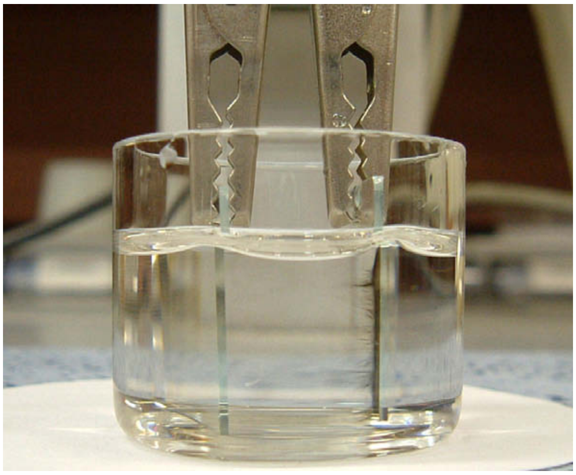

Fig. 3 – An optical image of the aligned SWCNTs deposited on positively charged ITO electrode surface in the presence of an electric field. The right electrode is the positively charged one in this image.

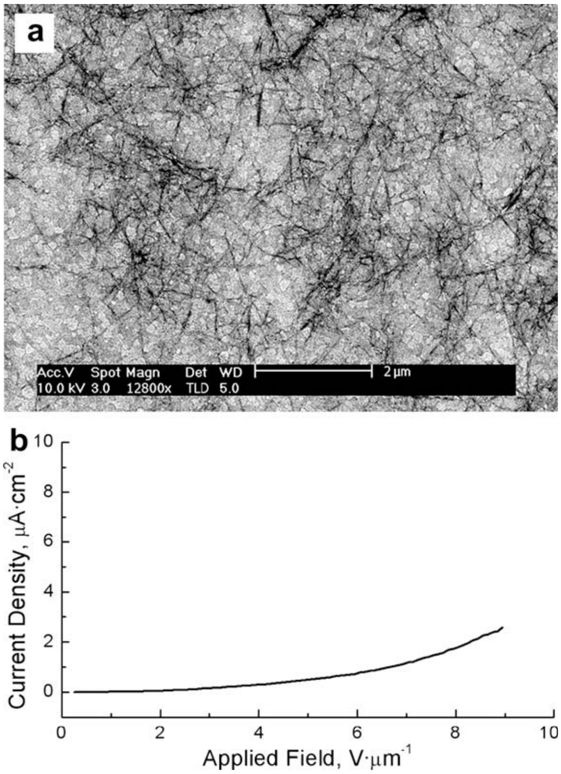

Fig. 4 – (a) An SEM image of SWCNT film deposited on ITO surface with no supporting colloidal frame and (b) a plot of the current density versus electric field for the field emission devices fabricated with such SWCNT films.

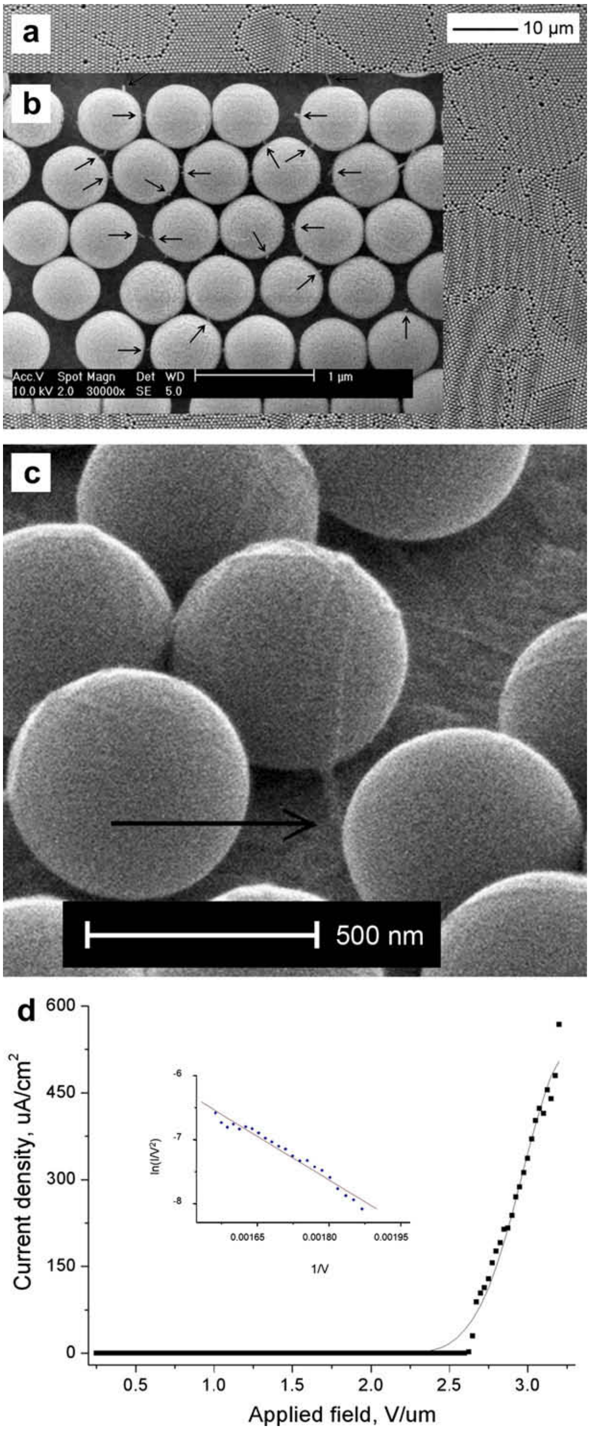

Fig. 5 – SEM images of (a) silica colloidal monolayer, (b) vertically aligned SWCNTs in the interstices of silica beads, (c) a titled image of a vertical SWCNT bundle, standing against a colloidal particle and attached on the ITO substrates and (d) field emission characteristics of a field emission device fabricated with such aligned SWCNTs, and the F–N plot in the inset.

Fig. 3, the SWCNTs are vertically deposited on the ITO surfaces with the induction effect of electric field (a solution with concentration less than 2 mg L^{-1} was used); moreover, the vertical alignment of the SWCNTs can be maintained in the interstices of the colloidal superlattices after the electric field is moved, as tips of tiny SWCNT bundles can be observed when viewed from the top of the assembly film (Fig. 5b). A tilted SEM image shows that the SWCNTs, standing against the colloidal particles, are directly anchored on the SAM-modified ITO substrates (Fig. 5c). Therefore, the silica beads play an important role in keeping SWCNTs vertically aligned onto the ITO surfaces.

The behavior of the aligned SWCNTs varies with both the size of silica beads and the concentration of the SWCNT solution. In our research, silica beads with diameter of 280, 570, and 730 nm were employed to fabricate the SWCNT assemblies. We found that the bead size shows remarkable influence on SWCNT deposition. 570 nm turns out to be the optimal diameter to obtain vertically aligned SWCNTs, as described above. On using silica beads of 280 nm in diameter, both vertically aligned SWCNTs and aggregated SWCNTs lying on the top of the colloidal monolayer are observed (Supporting Material S3). Finally, the monolayer of 730 nm silica beads cannot efficiently maintain the SWCNTs vertically aligned because of the bigger interstices. As for the influence of SWCNT concentration, the SWCNTs were found to be highly overlapped on the top of the colloidal superlattices (Fig. 6a), when a high concentration solution (more than 5 mg L^{-1}) was used, probably because more physical interconnections exist among the SWCNTs in such a solution. Similar to the field emission devices fabricated in the absence of colloidal superlattices, the devices fabricated with the overlapped SWCNTs show poor field emission property also (Fig. 6b).

On the other hand, the aligned SWCNTs in the interstices of the colloidal superlattices show notable improvement in field emission. Fig. 5d shows the change of field emission current density of a device fabricated with the vertically aligned SWCNTs as a function of the applied electric field. The threshold voltage (E_{th}) is measured to be 2.4 V μm^{-1}, and the emission current density of this device is found to be around 600 $\mu A\ cm^{-2}$ at a voltage of 3.2 V μm^{-1}. The field enhancement factor (β) is determined by using the Fowler–Nordheim (F–N) relationship: $\beta = B\phi^{3/2}d\ S^{-1}$, where $B = 6.83 \times 10^9$ ($VeV^{-3/2}\ m^{-1}$), ϕ represents the work function of SWCNTs and d represents the distance between the two electrodes. Therefore, β is calculated to be 3392 with an assumed work function of 5 eV for the SWCNTs (inset of Fig. 5d). The enhancement in the field emission is clearly due to the vertical alignment of the SWCNTs obtained with the supporting of silica beads, since the field emission devices fabricated in the absence of the colloidal monolayer show very weak field emission (Fig. 4b).

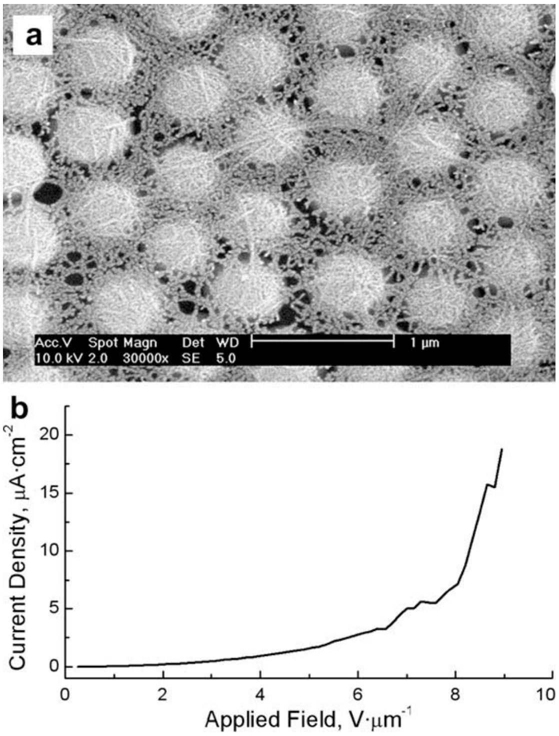

Fig. 6 – (a) An SEM image of overlapped SWCNTs formed with a high-concentrated SWCNT solution and (b) a plot of the current density versus electric field for the field emission devices fabricated with such SWCNT films.

It is worthy to note that the silica monolayer plays important roles in obtaining high field emission performance in two ways: keeping the SWCNTs vertically aligned as discussed above and preventing the SWCNTs densely aggregated. It was reported that the density of the SWCNTs plays a crucial role for field emission properties [34–36], and low density SWCNT films generate higher emission current, due to the avoidance of the screening effect. Fig. 1 illustrates geometric relationship between the interstice and bead size, from which we can qualitatively know the density of the interstice. Therefore, in our study, the high field emission property is attributed to both the vertical alignment of SWCNTs and low SWCNT density.

4. Conclusions

We have developed a new method for the fabrication of vertically aligned SWCNTs on SAM-modified ITO substrates by using a well dispersed SWCNT solution, a supporting frame composed of a monodispersed silica monolayer, and an AC electric field. The use of the colloidal monolayer as the supporting frame contributes to both the vertical alignment of the SWCNTs on the ITO substrate and the low density of the aligned SWCNTs, resulting in enhanced field emission. This approach can potentially lead to the application of SWCNTs as field emission sources in flat panel displays, as well as the possibilities of other techniques such as photolithographic and imprint lithographic approaches. Additionally, this method using a supporting frame to build vertically aligned SWCNTs has the following advantage: low CNT consumption, mild temperature condition, and large area deposition. Therefore, this method may open a new avenue for SWCNTs to mass application.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbon.2009.02.001.

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